Preparation and investigation of high purity Ge-Te-AgI glasses for optical application

V.S. Shiryaev[1], A.P. Velmuzhov[1], M.F. Churbanov[1], A.D. Plekhovich[1], C. Boussard-Plédel[2], J. Troles[2], C. Conseil[2], V.G. Plotnichenko[3]

1 - G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, 49 Tropinin Str., 603950 Nizhny Novgorod, Russia
2- Equipe Verres et Céramiques, Laboratoire Sciences Chimiques de Rennes UMR-CNRS 6226 Campus de Beaulieu, Rennes, France
3 - Fiber Optics Research Center of the Russian Academy of Sciences, Moscow, 119333, Russia
E-mail: shiryaev@ihps.nnov.ru

Keywords: Tellurium based chalcohalide glasses; Chemical-distillation purification; Infrared transmission; Crystallization

Abstract

The method for the preparation of high purity Ge-Te-AgI glasses with low content of limiting impurities has been developed. The method includes the synthesis of $GeTe_4$ glass using chemical distillation purification, loading AgI and $GeTe_4$ into silica glass reactor by evaporation in all-sealed glass vacuumed system, melting the $(GeTe_4)_{100-x}(AgI)_x$ (x=0-20) glass into muffle rocking furnace at 850^0C, quenching the glass in water with subsequent annealing and cooling.

The prepared glass samples were investigated by energy-dispersive X-ray microanalysis, DSC, FTIR-spectroscopy, Raman spectroscopy, and laser calorimetry.

The high purity $(GeTe_4)_{100-x}(AgI)_x$ (x=0-20) glass samples are characterized by good transparency in the spectral range of 2-20 μm, glass transition temperature of 140-160^{0}C, T_c-T_g difference of more than 100^0C, and a very low content of the limiting impurities. Some glass compositions with AgI content between 10 and 20 at.% manifest a good thermal stability against crystallization.

1. Introduction

In recent decade there is a great interest in Te-rich chalcogenide and chalcohalide glasses as a material transparent in the middle and far infrared ranges. Due to high atomic weight of tellurium chalcogenide $GeTe_4$-based glasses can transmit in the spectral range of 2- 25 μm and are the best candidates for systems operating in the mid-infrared range, including remote IR spectroscopy, thermal imaging, and CO_2 infrared detecting at wavelengths near 4.3 and 15 μm [1-3].

It is for the first time that the glass formation in binary Te-Cl, Te-Br, Te-I systems was described in paper [4]. These glasses demonstrate not only interesting optical properties but also a high tendency to crystallization, and poor mechanical and thermal characteristics. Therefore, their practical interest is very limited. The glass formation domain in the Ge-Te system extends from 10 up to 25 at.% of Ge, around the eutectic composition of about $Ge_{15}Te_{85}$. This glass composition has the local composition consisted of $GeTe_4$ tetrahedra linked by excess Te atoms which facilitate the

crystallization. $GeTe_4$ composition with the glass transition temperature $T_g=140^0C$ and the temperature of the onset of crystallization $T_c=217^0$ has the best glass-forming ability in Ge-Te binary system [5]. However, the T_c-T_g =77 ^0C difference is too small for this glass to be shaped without crystallization. It was found that addition of small amount of Ga to $GeTe_4$ alloy led to stabilization of glassy phase [1]. $Te_{75}Ge_{15}Ga_{10}$ ($T_c-T_g=113^0C$) was found to be a more stable composition in Te-Ge-Ga system. Unfortunately, due to the complexity of the purification process of Ga-containing glass, the optical losses in $Ge_{15}Te_{75}Ga_{10}$ optical fibers were very high [6].

An addition of small amount of Se (3-5 at.%) to $GeTe_4$ glass decreases a tendency to crystallization simultaneously maintaining the long-wavelength transparency region of pure germanium telluride glass. It was found that $Te_{76}Ge_{21}Se_3$ glass has T_c-T_g=115^{0}C [3] and it is acceptable for fiber drawing. It takes place despite the fact that the presence of only 3% Se in glass network causes an absorption band near 18 μm due to two-phonon absorption of Ge-Se bonds.

An addition of the iodine into germanium telluride breaks the Te-Te chains, improves the fragility of glass network and improves the glass stability [7]. Composition of $Te_{73}Ge_{20}I_7$ is in the middle of glassy domain in Te-Ge-I system and has a value of T_c-T_g=124^{0}C. Therefore, this glass is acceptable for molding and even for fiber drawing.

An addition of heavy metal halide AgI as a glass modifier instead of I_2 into the $GeTe_4$ glassy network is expected to improve the glass-forming ability, increase T_g and reduce the volatilization of iodine during the processes of glass melting and fiber drawing [8,9]. The paper [8] showed that an addition of up to 20 at. % of AgI to $GeTe_{4.3}$ glass increases the glass stability. According to data [9], in Ge-Te-AgI system the silver ions are likely to be in a tetrahedral environment of iodide ions, forming α-AgI-like tetrahedral clusters in the glass network. The three-dimensional AgI tetrahedral units play the role of a glass former and increase the cross-linking of glasses. The iodine atoms, forming covalent bonds with tellurium, decrease the concentration of Te-Te homoatomic bonds. This structural feature of Ge-Te-AgI glasses ensures a sufficient limitation of degree of freedom to prevent the rearrangement of glass network into regular crystalline structure. Therefore, the tendency to crystallization of Ge-Te-AgI glasses is lower in comparison with Ge-Te glasses. Nevertheless, the $GeTe_{4.3}$-AgI glasses of different compositions show crystallization during DSC analysis [8]. This can be caused by not only homogeneous mechanism of nucleation, but also heterogeneous crystallization on heterophase inclusions such as SiO_2, Al_2O_3, MgO or dispersed carbon.

In addition, the Ge-Te-AgI glasses, described in literature [8,9], are characterized by the presence of oxygen, water and Si-O impurities with their absorption bands in the middle infrared.

Therefore, the purpose of the work is the development of preparation method of Ge-Te-AgI glasses with low content of limiting impurities and with low tendency to crystallization.

2. Experimental

A series of Ge-Te-AgI glasses was prepared by traditional (direct synthesis from elements) and chemical-distillation methods. Preliminary the ampoules from silica glass were washed out in HF, distilled water, spirit and heated at temperature of 900^{0}C within 24 hours to remove the

hydrogen impurity. The granulated Ge with purity of 99.9999 %, tellurium with purity of 99.999 %, and AgI with purity of 99.9999 % were used.

Using the direct synthesis method from elements, the glass samples with compositions of $(GeTe_4)_{100-x}(AgI)_x$ (x=0-20) were prepared. The initial high-purity germanium, tellurium and AgI in the form of small pieces were loaded into silica ampoule for synthesis. Then the ampoule with the charge was evaporated at 10^{-7} torr, sealed from vacuum system and placed into the rocking muffle furnace. Then the ampoule was slowly heated up to the temperature of 850 ^{0}C and the charge was melted for 5 h. Later the melt was solidified in water from temperature of 650^{0}C with subsequent annealing at 130^{0}C (for 30 minutes) and slowly cooled to room temperature..

To prepare high-purity Ge-Te-AgI glass samples, a combination of chemical and distillation methods for purification of Ge-Te alloy and vacuum distillation of AgI were used [10,11]. Firstly, the high-purity GeTe alloy of given composition (close to $GeTe_4$) was obtained. For this, the chemical getter (500 ppm of Al) was added to the initial charge of Ge-Te mixture. The scheme of system for preparation of high-purity germanium telluride using oxygen getter is shown in Fig.1. The evacuated ampoule with the charge of Ge, Te and Al was mounted in the rocking muffle furnace, and the mixture was heated for 3 h up to 800^{0}C and melted at this temperature for 8-10 h. The oxygen impurity was transferred in low-volatile form (Al_2O_3). After, the ampoule was cooled and fused to the silica system for double distillation. The distillation of glass melt was carried out in the open and then closed vacuum systems sequentially at the temperature of evaporator of about 750^{0}C. After vacuum distillation, the ampoule-receiver of distillate of Ge-Te alloy was cooled down to room temperature. The second stage of Ge-Te-AgI glass purification included loading high-pure AgI into silica reactor in the all-sealed glass vacuum system. Then the silica reactor with $GeTe_4$ and AgI was sealed from the vacuum system and mounted in the rocking muffle furnace for synthesis. The Ge-Te-AgI charge was melted at 850^{0}C for 10-12 h. Then, the melt was solidified in water from the temperature of 600^{0}C with subsequent annealing at 140^{0}C for 30 min and slow cooled to the room temperature at the rate of 30 K/h.

The glass and residue compositions after distillation were examined by energy-dispersive X-ray microanalysis using a scanning electron microscope SEM-515 (Philips, the Netherlands) equipped with energy dispersive analyzer EDAX-9900 (EDAX, the USA). In addition, the chemical nature of glass residue was investigated by emission-spectral analysis.

The thermal analysis of glass samples (DSC) was carried out using a synchronous Netzsch STA 409 PC Luxx analyzer with sensitivity of 1 μV/mW and accuracy with respect to temperature ±1K.

To measure the optical transmission of the prepared glasses, the samples were cut, and the plate-parallel surface plates with a thickness of 2 - 10 mm were prepared. Glasses were analyzed by

IR-spectroscopy (IR-Fourier spectrometer IRP Prestige–21, Shimadzu, Japan) and Raman scattering. The content of impurities (oxides, CO_2 and water) was determined by comparing the absorption bands with the molar extinction coefficients reported in the literature: $\varepsilon(CO_2)$= 15.6 dB/m/ppm at 4.33 μm As-S glass [12] . ε(Ge-O)= 2.6 dB/m/ppm at 7.9 μm wavelength for Ge-As-Se-Te glass [13], $\varepsilon(H_2O)$= 34 dB/m/ppm at 6.3 μm for silicate glass [14].

The method of thermometric laser calorimetry [15] was used to determine the bulk absorption coefficient of high-pure glasses at wavelength of 10.6 μm. This method is based on measurement and analysis of the heating of cylindrical glass rods caused by the absorption of the transmitted laser radiation.

The presence of crystalline phases in glasses was controlled by X-ray diffraction analysis with XRD-6000 Shimadzu difractometer using CuK_α radiation.

The possible local structure of $GeTe_4$ network, modified by AgI addition, was investigated by a quantum chemistry method.

3. Results and discussion

3.1. Glasses prepared by direct synthesis from elements

Fig.2a shows DSC thermograms of $(GeTe_4)_{100-x}(AgI)_x$ (x=0-20) glasses prepared by direct synthesis from elements. The DSC measurements for glasses containing 10-20 at.% of AgI were stopped at the temperature of 360-380^{0}C due to volatilization of iodides. All studied samples are characterized by low-temperature endo-thermal effect connected with glass transition. The T_g value for these glasses is decreased from 148^{0}C for $GeTe_4$ to 134 ^{0}C for $(GeTe_4)_{80}(AgI)_{20}$. Thermograms of $GeTe_4$ and $(GeTe_4)_{95}(AgI)_5$ glasses show a single exothermal peak due to crystallization. When the AgI content in glass increases, the difference between the glass transition temperature and the temperature of the onset of crystallization increases as well. Glasses with 10-20 % AgI content do not show crystallization peaks, and manifest small high-temperature endo-thermal effect.

The drastic reduction of weight of AgI-contained glasses during DSC measurement at the starting temperature of 320-330^{0}C (by 1% for temperature interval of 40^{0}C) was observed (Fig.2b). It was determined that these weight changes were predominately due to evaporation of volatile GeI_4 during melting. The experiment of $(GeTe_4)_{85}(AgI)_{15}$ glass sample treatment at the temperature of 290^{0}C has shown the volatilization of GeI_4 compound in quantity of 1.5-2 % for 3 h. The endothermic variations around 320^{0}C in the DSC thermograms of AgI-containing glasses are related to this volatilization. In case of $GeTe_4$ glass, the weight change was not observed.

Fig.3 shows the transmission spectra of $(GeTe_4)_{100-x}(AgI)_x$ glass samples with thickness of 4.3 mm prepared by direct melting of initial special pure elements. It is seen that when the AgI content increases, the glass transparency becomes better, that is likely to be related to improvement of glass-forming ability. When these glasses were produced without special purification, the

transmission spectra contained impurity absorption bands: at 7.9 μm and 12.9 μm – due to Ge-O bonds, at 2.8 μm and 6.3 μm – due to water, at 4.3 μm – due to CO_2. All of these impurities are characteristic for glass samples obtained by direct synthesis of the elements. Their sources are oxides and carbon in the starting materials. Absorption band at wavelength of 23 μm is caused by intrinsic Te-Te bonds. The estimated content of impurities in various glasses is as following: oxygen in the form of Ge-O - 15-30 ppm wt, water - 10-18 ppm wt, CO_2 – 10-15 ppm wt.

3.2. Glasses, prepared by chemical-distillation method of purification

The glass samples, prepared using chemical-distillation purification, were in the form of rods with diameter of 7 mm and length of 100 mm, and had black shine color with glassy fracture.

The initial glass composition for synthesis was: $(GeTe_4)_{90}(AgI)_{10}$ for samples 1-3 and $(GeTe_4)_{85}(AgI)_{15}$ for samples 4 and 5. After distillation the initial glass composition was changed, and the result on composition is given in Table 1. The observed change in the initial glass composition depends on the distillation degree of Ge-Te and AgI compounds. Glasses 1 and 2 have the compositions which are more different from the given ones.

The cube residue after distillation of $GeTe_4$ melt was a dark grey powder consisting of particles with a size of several or tens microns. The weight of cube residue after first distillation was about 45 mg, while the weight of Ge-Te alloy was 25 g. It was determined that the inclusions mainly comprised approximately 80-90 % of Al, 10-15 % of Si, and 3-5 % of Ge and Te. The aluminum nature of non-volatile residue after glass distillation make it possible to assume that the inclusions mainly consist of aluminum oxide. It was due to bonding of the chemical getter (Al) with the impurity oxygen and the formation of low-volatile Al_2O_3. The presence of silicon impurity in the residue is connected with its entering from the walls of silica ampoule. The source of this contamination are the mechanical disintegration of SiO_2 amorphous layer on the inner surface of silica ampoule, and the chemical reactions of interactions of charge compounds, impurities and getter with silica glass.

DSC data of some glass samples are given in Fig.4 and Table 1. The sample 1 has low value of T_g (120^0C) and small difference of T_c-T_g (72^0C) due to high content of Te (81.1 at.%). Glasses 2 and 3 with 5-10 % of AgI show crystallization peak, and their difference in T_c-T_g is 91 and 105 ^{0}C, respectively. Glass 3 has a composition close to $(GeTe_4)_{90}(AgI)_{10}$, but with small excess of tellurium which can lead to crystallization of this glass during DSC analysis. Glasses 4 and 5 with compositions close to initial ones do not show crystallization peaks at heating rates of 10 and 2.5 K/min. It is evidence to their stability against crystallization.

Fig. 5a gives the transmission spectra of high-purity glasses 2-5 with thickness of 2 mm. All

these glasses do not show impurity absorption bands, and their transparency ranges stretch from 2 to 29 μm. The absorption band at 23 μm is caused by intrinsic 2-phonon absorption of Te-Te bonds. The slope of transparency curve for sample 2 in the range of 2-7 μm can be due to scattering by micro-inclusions in glass volume. Samples with 30-40 mm thickness have a good transparency in the mid-infrared as well. For example, Fig.5b gives the transmission spectrum of sample 4 with 31.2 mm thickness. The estimated content of oxygen in the form of Ge-O does not excess 0.3 ppm wt.

The low content of impurities in these glasses was achieved by using the combination of chemical and distillation methods for melt purification. The addition of small amount of Al to the charge is effective for removal of oxide impurities. Aluminum and oxides interact with the formation of low-volatile aluminum oxides. Distillation with low evaporation rate is effective at purification from the formed Al_2O_3 inclusions. As a result, the oxygen content in the prepared glass was very low.

The level of transparency of prepared glasses was investigated by the method of laser thermometric calorimetry. The lowest value of bulk absorption coefficient of 0.7 dB/m at wavelength of 10.6 μm was achieved in sample 4 (Fig.5b). The value is slightly limited by absorption band centered about 14 μm due to impurity or/and intrinsic vibrations. The bulk absorption coefficient characterizes the level of intrinsic optical losses, homogeneity (presence of inclusions, microcrystals and striaes) and purity (content of dissolved limiting impurities) of glass, particularly in the high transparency range. The measurements of infrared glasses made at the CO_2 laser wavelength of 10.6 μm allow to determine the excess of the fundamental absorption above the calculated value and to judge the purity and perfection of this material. The measured absorption coefficient value of 0.7 dB/m is one of lowest results on transparency for glassy materials obtained at 10.6 μm wavelength. This low value is encouraging and gives a hope to achieve in fibers based on these Ge-Te-AgI glasses the optical losses of 1 dB/m or lower in the CO_2 laser generation range.

3.3. Structural investigations

All prepared GeTe-AgI glasses were studied by the methods of Raman scattering and X-ray diffraction.

Fig.6 gives Raman spectra for 3 samples of Ge-Te-AgI glasses as well as for $Ge_{21}Se_3Te_{76}$ glass. All spectra have three distinct peaks centered at 90, 120 and 140 cm^{-1}. The first and the second peaks are assigned to Ge-Te bonds, the third – to Te-Te bonds [7,13]. The glasses without AgI also show additional broad band at 159 cm^{-1}, assigned to vibration of Te-Te bonds [13]. In AgI-contained glasses, this band at 159 cm^{-1} is very weak. According to data [16], the addition of iodine can open up Te-Te bonds and decrease the intensity of 159 cm^{-1} Te-Te vibrations. The

intensity of 140 cm^{-1} band remains almost unchanged in all Ge-Te-AgI glasses. The formation of Ag-Te bonds causes the increase in intensity of Ge-Te bonds at 90 cm^{-1} and 120 cm^{-1}. These observed results were confirmed by theoretical calculation of possible local structure of $GeTe_4$ -AgI glass network by a quantum chemistry method. The model $GeTe_4$-AgI glass network has shown that the iodine atoms are incorporated into glass structure breaking Te-Te bonds, which should lead to decrease in intensity of their vibration bands. The calculated Raman activity spectrum, obtained from the model glass network (Fig.6), is very close to experimental Raman spectra.

Fig. 7 shows X-ray diffraction patterns of some Ge-Te-AgI samples. All as-received glasses are in the amorphous state as it is shown in Fig.7a. It confirms the amorphous nature of the prepared glasses. However, the isothermal treatment of these glasses causes crystallization. Fig. 7b shows a small intensity peak of Te crystalline phase in glass 4 when it was annealed near the temperature of 290^0C for 20 min. Treatment of glass samples at this temperature for 3 h causes the formation of crystalline phases: Te, GeTe and γ-AgI (Fig.7c). Thus, though $(GeTe_4)_{90}(AgI)_{10}$ and $(GeTe_4)_{85}(AgI)_{15}$ glasses do not show crystallization during DCS analysis and have the amorphous nature at ambient temperature, they are unstable at high-temperature treatment. In addition, we observed crystallization of these GeTe4-AgI glasses during fiber drawing from crucible or rod. Thus, to prepare the optical elements (lenses, prisms, fibers) from these glasses, some special time-temperature conditions are necessary to decrease the glass crystallization.

The calculation of the composition of equilibrium phases in Ge-Te-AgI system was carried out by the method of equilibrium constants [17] using the standard thermodynamic functions of substances [18] (Fig.8). The initial proportion of components corresponded to $(GeTe)_{90}(AgI)_{10}$ glass composition. According to the calculation results, the main components of melt are as following: tellurium in condensed Te(c) and gaseous Te(g) phases, condensed phase of germanium telluride GeTe(c), and condensed phase of silver iodide AgI(c). The calculated content of GeI_4 is 0.01-0.1 mol.%, the content of I_2, TeI_4 and Ag_2Te in the system is negligibly small. The results of thermodynamic calculation are in good agreement with the experimental data of x-ray diffraction analysis of the crystallized glasses (Fig.7).

4. Conclusions

A series of $GeTe_4$-AgI glasses was prepared by traditional and chemical-distillation methods. Some glass compositions with AgI content between 10 and 20 at.% manifest a good thermal stability against crystallization. The preparation method of high-purity $GeTe_4$-AgI glasses with low

impurity content has been developed. High purity $GeTe_4$-AgI glass samples are characterized by good transparency in the mid-infrared, low content of limiting impurities and absence of oxide and water absorption bands in transparency spectra. The addition of AgI to $GeTe_4$ glass improves the transparency and decreases the tendency to crystallization. Glasses containing 10-20 % of AgI do not show crystallization peaks on DSC thermograms at heating rates of 10 and 2.5 K/min. The value of bulk absorption coefficient determined by laser calorimetry at wavelength of 10.6 μm was 0.7 dB/m. This very low magnitude of absorption in Ge-Te-AgI glass prepared using chemical and distillation methods of purification is an evidence of low intrinsic optical losses, high optical homogeneity and purity of this glass. To prepare the optical fibers from these glasses, some special time-temperature conditions are necessary to decrease the glass crystallization.

Acknowledgments

This work was financially supported by the Russian Foundation for Basic Research (project no. 13-03-01091). The authors wish to thank A.I. Suchkov, M.V. Sukhanov, A.A. Pushkin and V.V. Koltashev for their contribution to the investigation of glass samples.

References

[1] S. Danto, P. Houizot, C. Boussard-Pledel., X.-H. Zhang, F. Smektala, and J. Lucas, Adv. Funct. Mater. **16** (2006) 1847-1852.

[2] B. Bureau, S. Danto, H. Ma, C. Boussard-Pledel, X.H. Zhang, J. Lucas, Solid State Sci. **10** (2008) 427-433.

[3] S. Maurugeon, C. Boussard-Pledel, J. Troles, A.J. Faber, P. Lucas, X.H. Zhang, J. Lucas, and B. Bureau, J. Lightwave Technology, **28** (2010) 3358-3363.

[4] J. Lucas, X.H. Zhang, Mater. Res. Bull. **21** (1986) 871-876.

[5] L. Kaltenegger, C.V.M. Fridlung, J. Adv. Space Res. **36**(2005) 1114-1122.

[6] S. Zhang, X. H. Zhang, M. Barillot, L. Calvez, C. Boussard, B. Bruno, J. Lucas, V. Kirschner, G. Parent, Opt. Mater. **32**(2010) 1055-1059.

[7] A. Wilhelm, C. Boussard-Pledel, Q. Coulombier, J. Lucas, B. Bureau, P. Lucas, Adv. Mater. **19** (2007) 3796-3800.

[8] X. Wang, Q. Nie, G. Wang, J. Sun, B. Song, S. Dai, X. Zhang, B. Bureau, C. Boussard, C. Conseil, H. Ma, Spectrochim. Acta Part 1, **86** (2012) 586-589.

[9] Q. Nie, G. Wang, X. Wang, S. Dai, S. Deng, T. Xu, X. Shen, Opt. Commun. **283** (2010) 4004-4007.

[10] V.S. Shiryaev, J.-L. Adam, X.H. Zhang, C. Boussard-Plédel, J. Lucas and M.F. Churbanov. J. Non-Cryst. Solids. **336** (2004) 113-119.

[11] V.S. Shiryaev, M.F. Churbanov, E.M. Dianov, V.G. Plotnichenko, J.-L. Adam, J. Lucas, J. Optoelectron. & Adv. Mater **7**(4) (2005) 1773-1779.

[12] G.E. Snopatin, V.S. Shiryaev, G.E. Plotnichenko, E.M. Dianov, M.F. Churbanov, Inorg. Mater. **45**(13) (2009) 1439-1460.

[13] J. Nishii, T. Yamashita, and T. Yamagishi, J. Mater. Sci. **24** (1989) 4293-4297.

[14] F.M. Ernsberger, J. Amer. Ceram. Society **60** (1977) 9l-92.

[15] V.G. Plotnichenko, V.K. Sysoev, I.G. Firsov, Kvantov. Electron. **8**(7) (1981) 1495-1503 (in Russian)

[16] J. Sun, Q. Nie, X. Wang, S. Dai, X. Zhang, B. Bureau, C. Boussard, C. Conseil, H. Ma, Infrared Physics & Technology **55**(2012) 316-319.

[17] A.P. Velmuzhov, A.A. Sibirkin, V.S. Shiryaev, M.F. Churbanov, J. of Optoelectron. & Adv. Mater. **13**(11–12) (2011) 1437-1441.

[18] I. Barin, Thermochemical data of pure substances, New York, 1995. 1885 p.

Captions

Fig.1. Set-up for preparing high purity Ge-Te glass: 1 – ampoule with Ge-Te melt after interact with Al getter; 2 – intermediate ampoule; 3 – synthesis reactor; 4 – trap for light volatile impurities; 5 – glass partition; 6 – magnetic hammer-breaker; 7 –glass tube; 8 – wire heater; 9 - furnace

Fig.2. (a) DCS termograms of $GeTe_4)_{100-x}(AgI)_x$ (x=0-20) glasses prepared by direct melting from elements; (b) Weight change of glass during DSC measurement

Fig.3. Transmission spectra of $(GeTe_4)_{100-x}(AgI)_x$ glass samples (thickness is 4.3 mm) prepared by direct melting initial special pure elements

Fig.4. DSC thermograms of high-purity Ge-Te-AgI glasses prepared by chemical distillation method

Fig.5. (a) Transmission spectra of high-purity Ge-Te-AgI glass samples (thickness is 2 mm); (b) Transmission spectrum of glass 4 with thickness of 31.2 mm (this sample was used for determination of volume absorption coefficient)

Fig.6. Raman spectra of $GeTe_4$-based glasses

Fig.7. The X-ray diffraction pattern of (a) as-received glasses; (b) glass 4 after thermal treatment at 290^0 for 20 min; (c) glass 4 after thermal treatment at 290^0 for 3 h

Fig.8. Thermodynamically calculated composition of condense and gaseous phases for $(GeTe_4)_{90}(AgI)_{10}$ glass

Table 1. Glass compositions and thermal points of prepared high-purity samples

Glass sample	1	2	3	4	5
Initial glass	$(GeTe_4)_{90}(AgI)_{10}$			$(GeTe_4)_{85}(AgI)_{15}$	

composition					
Glass composition after distillation	$Ge_{14.7}Te_{81.3}(AgI)_{3.2}I_{0.8}$	$Ge_{17.9}Te_{76.8}(AgI)_{4.8}I_{0.5}$	$Ge_{16.1}Te_{73.7}(AgI)_{10.2}$	$Ge_{16.7}Te_{67.2}(AgI)_{15.6}Ag_{0.5}$	$Ge_{16.6}Te_{66.3}(AgI)_{15.8}I_{1.3}$
T_g, ^0C	120	138	130	136	134.5
T_c, ^0C	192	243	221	no	no
T_c-T_g, ^0C	72	105	91		
T_x, ^0C	214	250	250		

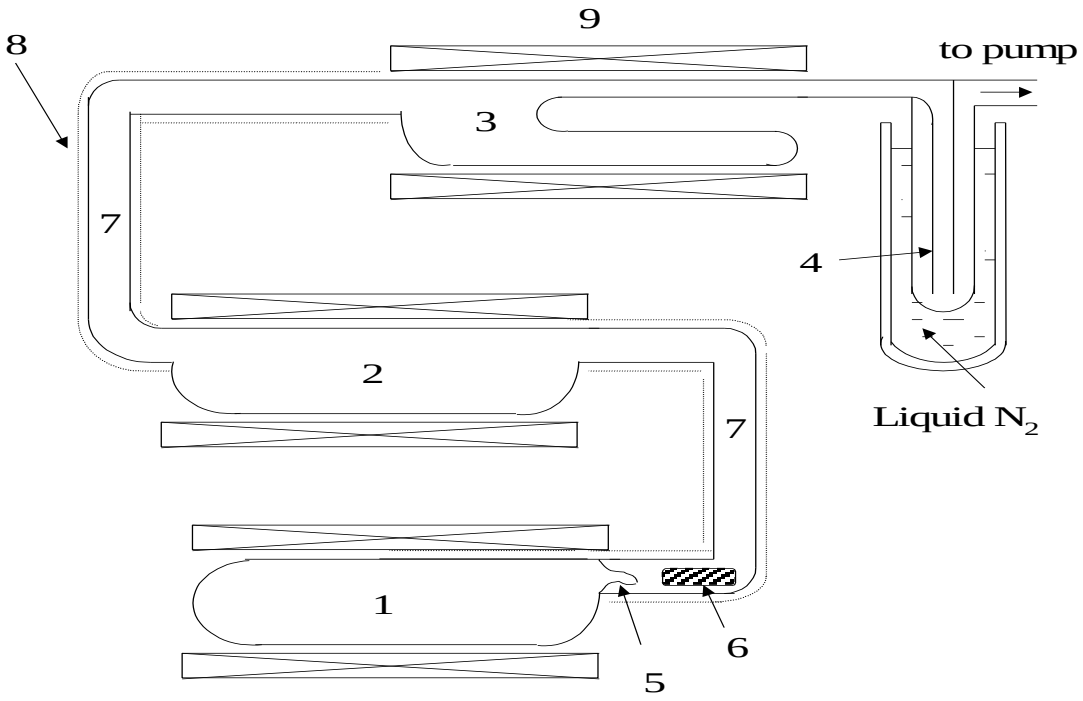
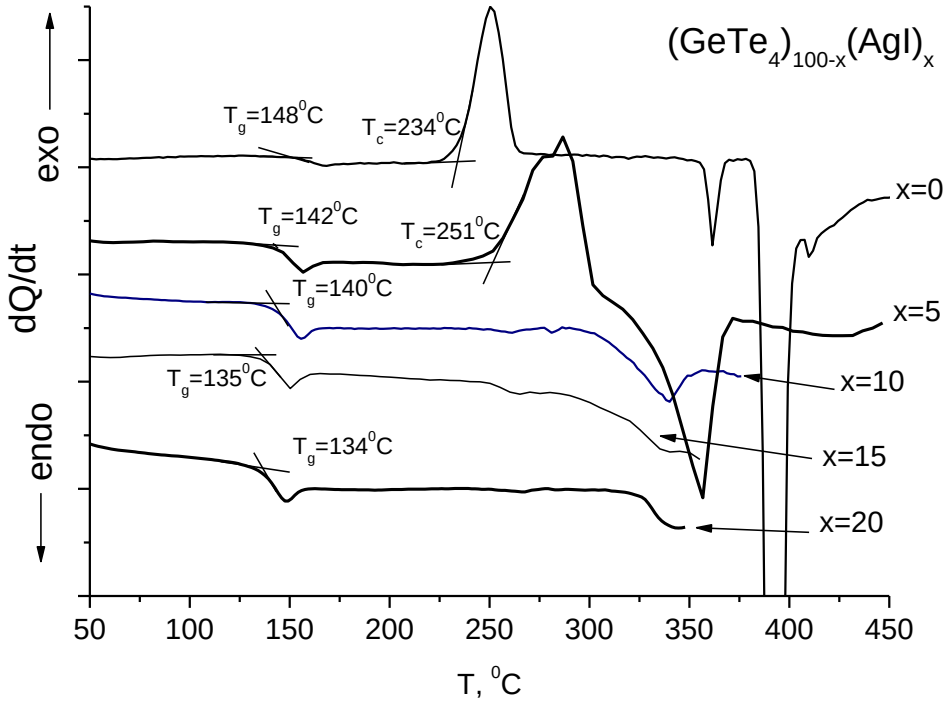
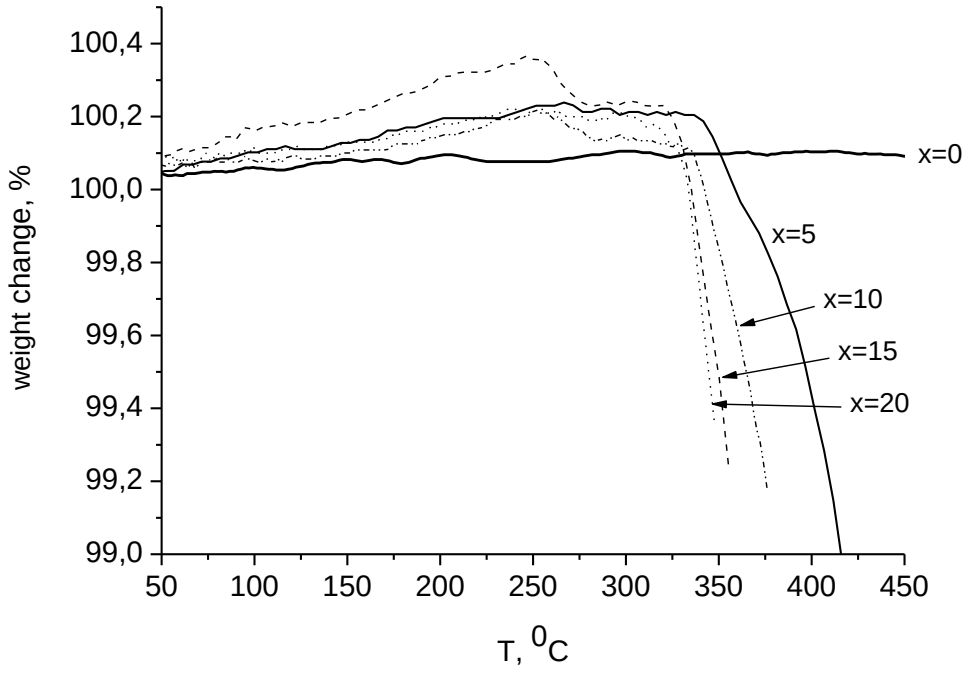


Fig.1. Set-up for preparing high purity Ge-Te glass: 1 – ampoule with Ge-Te melt after interact with Al getter; 2 – intermediate ampoule; 3 – synthesis reactor; 4 – trap for light volatile impurities; 5 – glass partition; 6 – magnetic hammer-breaker; 7 –glass tube; 8 – wire heater; 9 - furnace



a



b

Fig.2. (a) DCS termograms of $GeTe_4)_{100-x}(AgI)_x$ (x=0-20) glasses prepared by direct melting from elements; (b) Weight change of glass during DSC measurement

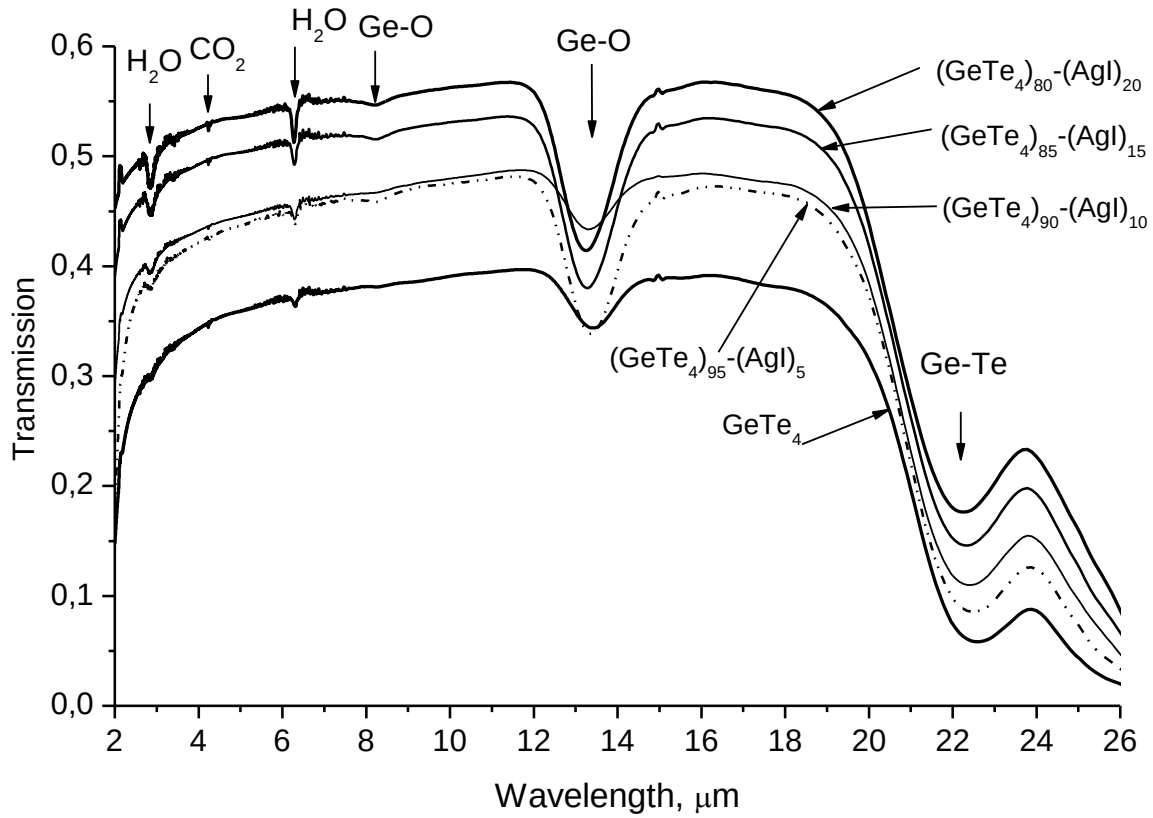


Fig.3. Transmission spectra of (GeTe4)100-x(AgI)x glass samples (thickness is 4.3 mm) prepared by direct melting initial special pure elements

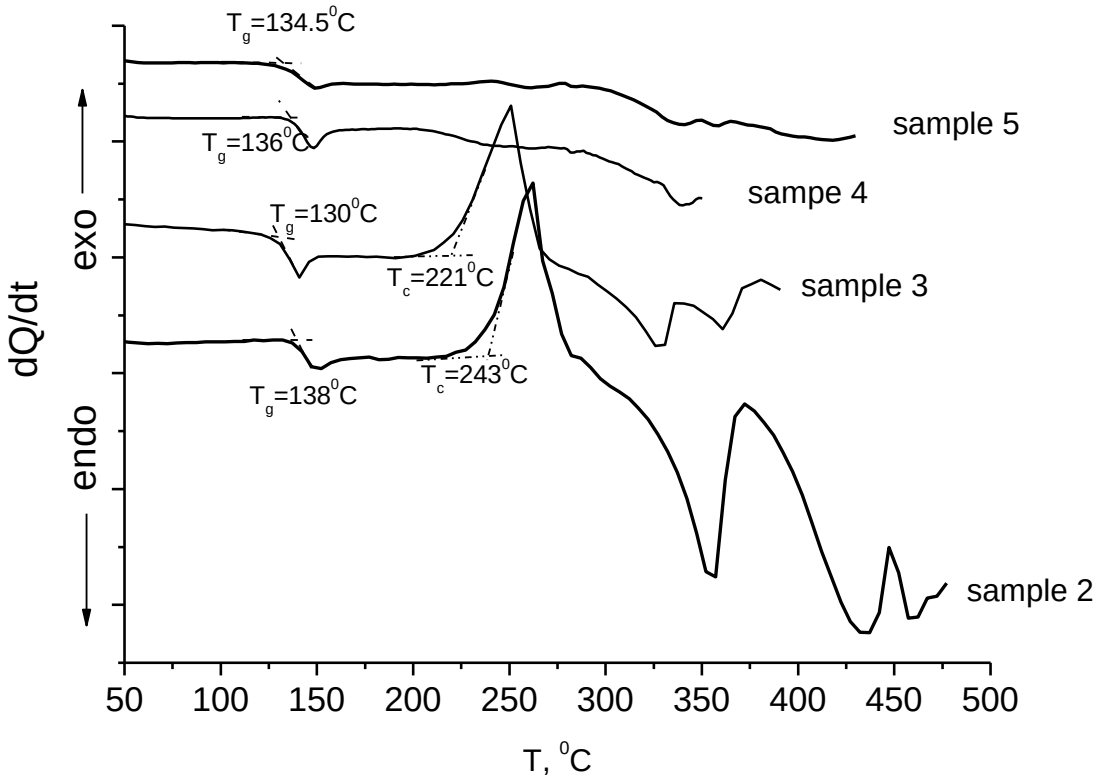
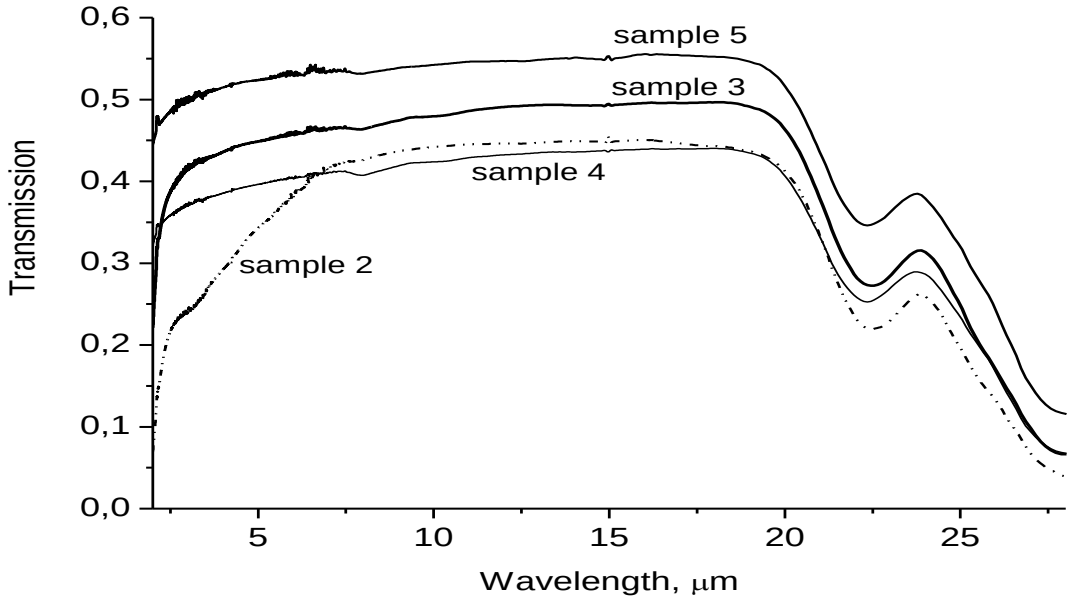
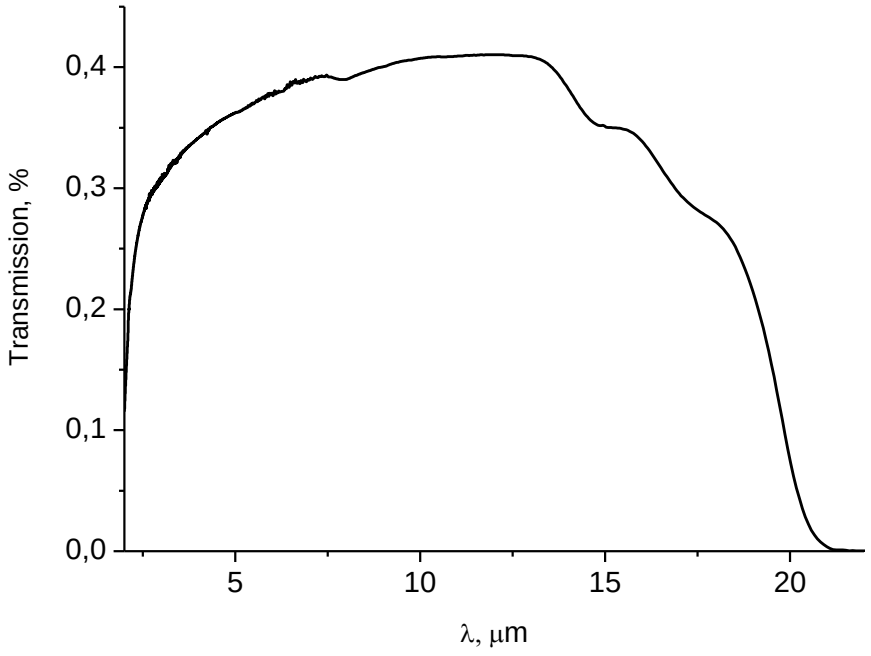


Fig.4. DSC thermograms of high-purity Ge-Te-AgI glasses prepared by chemical distillation method





b

Fig.5. (a) Transmission spectra of high-purity Ge-Te-AgI glass samples (thickness is 2 mm); (b) Transmission spectrum of glass 4 with thickness of 31.2 mm (this sample was used for determination of volume absorption coefficient)

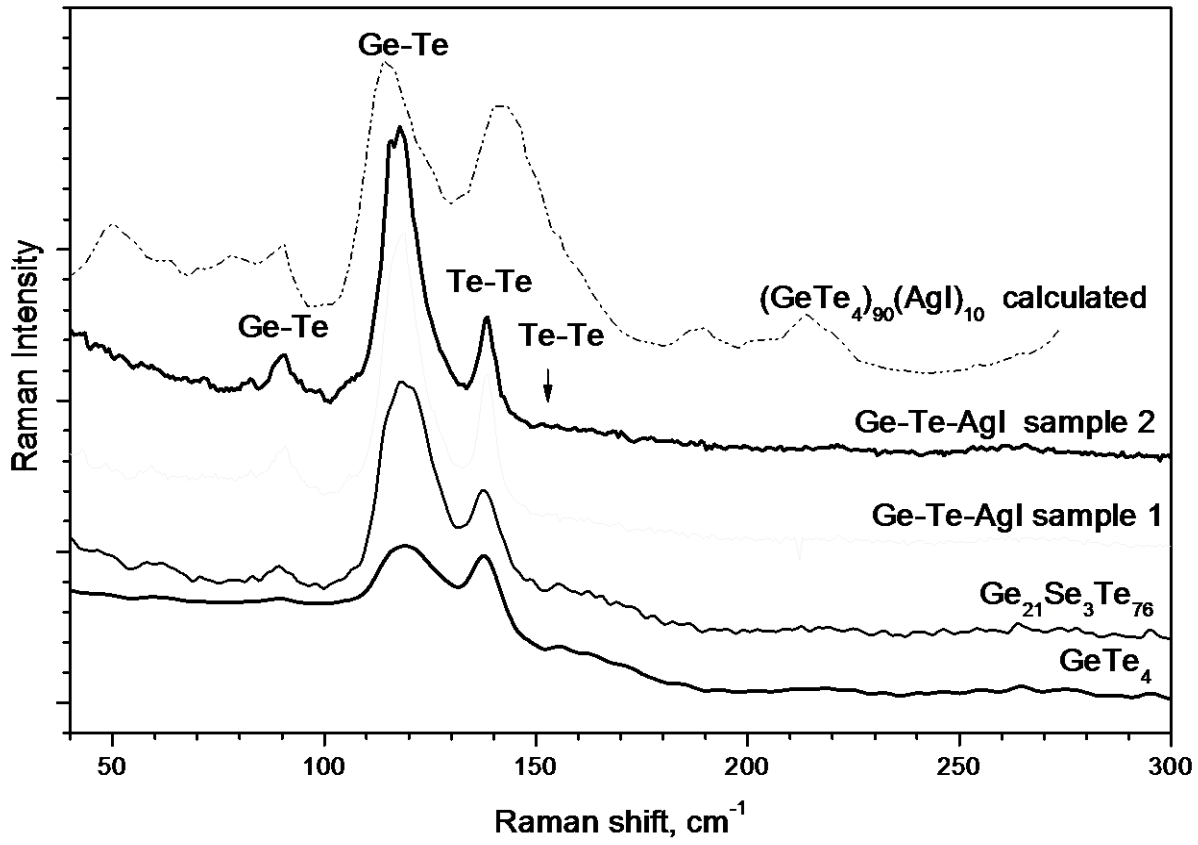


Fig.6. Raman spectra of $GeTe_4$-based glasses

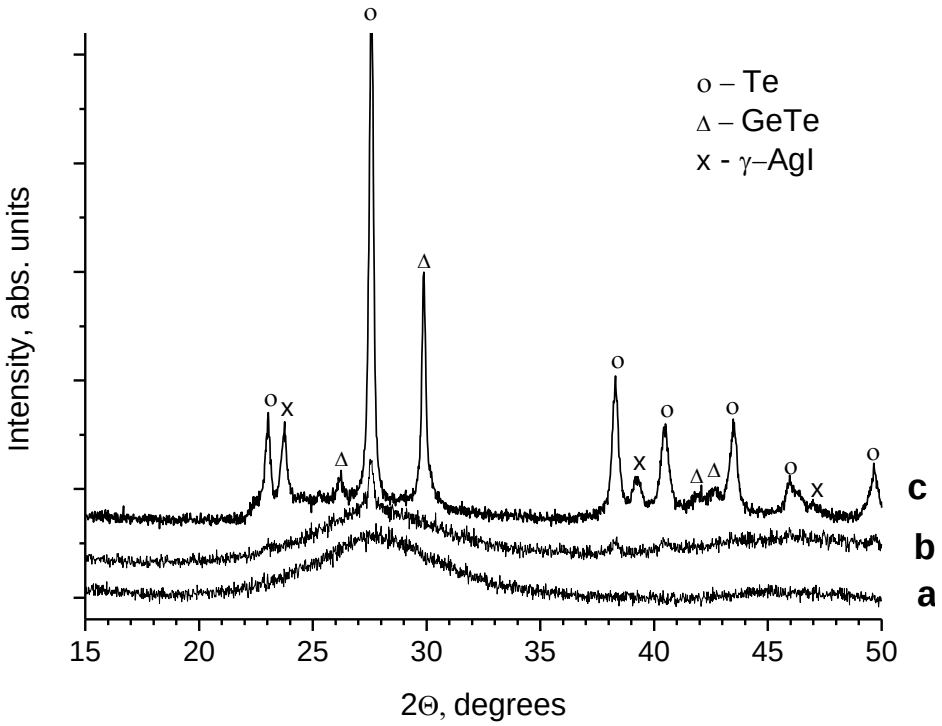


Fig.7. The X-ray diffraction pattern of
(a) as-received glasses
(b) glass 4 after thermal treatment at 290^0 for 20 min;
(c) glass 4 after thermal treatment at 290^0 for 3 h

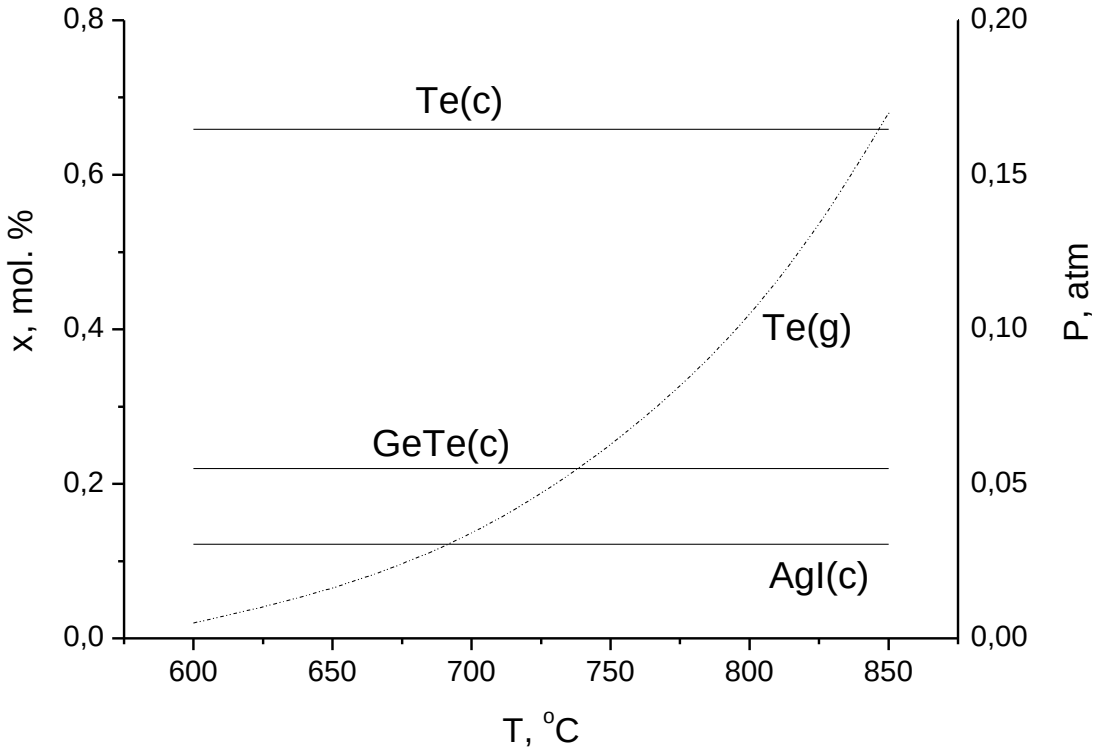


Fig.8. Thermodynamically calculated composition of condense and gaseous phases for $(GeTe_4)_{90}(AgI)_{10}$ glass